

On the energy of activation for self-diffusion in metals

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With 1 figure in the text

The mechanism of lattice diffusion that seems to be best consistent with our collected experimental knowledge of the metals is that the thermal density fluctuations open up voids between the atoms, big enough for one of the adjacent atoms to jump into it and that after such a jump the lattice rearranges itself, the net result being a change in the mutual arrangement of a few atoms. Such a mechanism is also well compatible with a difference in the rate of transport of different atoms in an alloy and thus with the Kirkendall effect. In the present paper we shall, however, confine ourselves to self-diffusion in pure metals.

The initiating moment of the process is thus supposed to be the creation of a void of the volume w of an atom and the potential energy u to be stored up in the surroundings of the lattice for this creation is the energy of activation for an elementary process. Referred to a mole, the energy of activation is

$$E = N u \quad (1)$$

where N is the number of atoms of a mole. w is known approximately, and we should be able to calculate the energy of activation if we could find the relationship between u and w . As the local increase of volume w is supposed to be a result of density fluctuations the energy u must also imply the energy of lattice contractions in the neighbourhood.

Now it has been shown in two recent papers (1, 2) that the ratio of the mean increase of potential energy and the mean increase of volume due to combined density fluctuations of both signs, the ratio $\Delta U / \Delta V$, is a very significant feature of the lattice, influencing the change of state on compression, on the thermal expansion of solid and liquid and on fusion. The present writer has therefore looked for a relationship between u/w on one side and $\Delta U / \Delta V$ on the other. It has not been possible so far to derive a relationship mathematically on basis of fluctuation statistics but it has been found by trial, that the simple relation

$$\frac{u}{w} = \frac{\Delta U}{\Delta V} \quad (2)$$

leads to very satisfactory agreement with experimental result. A combination of the equations (1) and (2) gives

$$E = \frac{\Delta U}{\Delta V} N w. \quad (3)$$

For w we have to choose the smallest volume that can admit an atom. The opening of larger voids will need a higher energy of activation, and as the frequency of a certain occurrence of this kind decreases very rapidly with increasing energy of activation the lowest value of w will be the decisive one. Thus w is probably the volume of the core of the atoms. An apparent value of this volume can be obtained from the compressibility formula introduced in an earlier paper (1)

$$(\Delta p + \alpha) (\Delta V + \beta) = \alpha\beta \quad (4)$$

where Δp and ΔV are combined variations of pressure and volume, and α and β are pressure and volume parameters characteristic of the metal. V and β are suitably referred to one mole. With increasing pressure the decrease of volume approaches the value $-\Delta V = \beta$, and $V - \beta$ thus represent the volume of the cores of the atoms of one mole. We thus have

$$N w = V - \beta. \quad (5)$$

Introduced in equation (3) this gives

$$E = \frac{\Delta U}{\Delta V} (V - \beta). \quad (6)$$

This equation can be used to evaluate the energy of activation E from experimental data of various kinds. The formula

$$\frac{\Delta U}{\Delta V} = \frac{3}{2} \alpha \quad (7)$$

deduced in an earlier paper (1) transforms equation (6) into

$$E = \frac{3}{2} \alpha (V - \beta) \quad (8)$$

which enables the calculation of E solely from compressibility data. As such data are not yet very accurately known we prefer determining E from equation (6) using calorimetric and dilatometric data.

A suitable measure of the potential energy U is, as shown in an earlier paper (2) the total energy minus the kinetic energy expressed by a Debye function, that is

$$U = \int_0^T C dT - \frac{3}{2} R T D\left(\frac{T}{\theta}\right) \quad (9)$$

where C is the molar heat at low pressure, T the absolute temperature, R the gas constant, θ the Debye characteristic temperature determined from specific heat at low temperatures, and

$$D\left(\frac{T}{\theta}\right) = 3 \left(\frac{T}{\theta}\right)^3 \int_0^{\frac{\theta}{T}} \frac{x^3 dx}{e^x - 1} \quad (10)$$

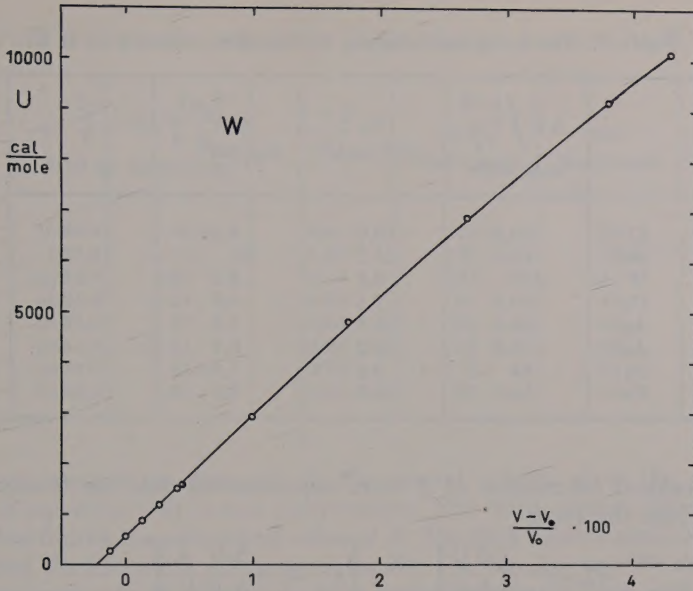


Fig. 1. Potential energy versus thermal change of volume for tungsten.

is a Debye function going from 0 to 1 with increasing value of T/θ . By means of these equations and tables for the Debye function, numerical values of U have been obtained for different temperatures from calorimetric data.

A plot of U versus the volumes for corresponding temperatures as shown in Fig. 1 for tungsten can be used for the determination of $\Delta U/\Delta V$. As the slope of the curve decreases slightly with increasing volume we conclude from equation (6) that the energy of activation E varies slightly with temperature. In order to obtain from equation (6) values of E that are comparable with the values obtained from diffusion measurements, we therefore have to determine the slope $\Delta U/\Delta V$ from a part of the curve corresponding to the range of temperature for these diffusion measurements.

The second factor $(V - \beta)$ in equation (6) is the volume of the atom cores in a mole. It can be supposed to be independent of temperature and thus determinable for instance at 0°C . As shown earlier (1) β can be replaced by

$$\beta = V\alpha\kappa = \frac{2}{3}V\frac{\Delta U}{\Delta V}\kappa \quad (11)$$

where κ is the compressibility coefficient. Equation (11) presupposes the use of rational units. If, in order to use data from the literature, we take U in calories pro mole, V in cm^3/mole and κ in $(\text{kp}/\text{cm}^2)^{-1}$ we have

$$\frac{\beta}{V} = 28.4 \frac{\Delta U}{\Delta V} \kappa. \quad (12)$$

Table 1. Data for calculation of the free volume at 0°C.

	$\Delta U / \frac{\Delta V}{V_0}$ kcal/mole	V_0 cm ³ /mole	$\kappa 10^6$ (kp/cm ²) ⁻¹	$\frac{\beta}{V}$ at 0°C
Li	20.3	13.0	8.8	0.39
Na	18.0	23.7	15	0.32
W	264	9.6	3.2	0.25
Cu	60.5	7.1	0.8	0.19
Ag	59.6	10.2	1.0	0.16
Au	73.3	10.2	0.7	0.14
Al	43	9.9	1.4	0.17
Pb	38.5	18.3	2.5	0.15

For a convenient calculation of E from experimental data we finally transform equation (6) into the form

$$E_{\text{at } t^\circ\text{C}} = \left[\frac{\Delta U}{\frac{\Delta V}{V_0}} \right]_{\text{at } t^\circ\text{C}} \times \left[1 - 28.4 \frac{\Delta U}{\frac{\Delta V}{V_0}} \frac{\kappa}{V_0} \right]_{\text{at } 0^\circ\text{C}} \quad (13)$$

which also enables us to refer all changes of volume to the volume V_0 at 0°C, as is usually done.

For the evaluation of E by means of equation (13) we need, apart from the compressibility coefficient κ , only diagrams like that of figure 1 for U as a function of $(V - V_0)/V_0$. In the following we shall confine ourselves to eight cubic metals for which the activation energies for self-diffusion are determined more or less accurately, namely, the body-centered cubic metals Li, Na, and W, and the face-centered Cu, Ag, Au, Al, and Pb. For all these metals except Li and W diagrams of U as a function of $(V - V_0)/V_0$ are given, together with references to the experimental sources, in the preceding paper (2). The diagram for W in Fig. 1 is based on tables of specific heat at low temperatures by Kelley (3) and at high temperatures by Stull and Sinke (4). The thermal expansion data are from Hidnert and Sweeney (5) up to 500°C, and from Worthing (6) for higher temperatures. For a diagram for Li we have again used the tables of calorimetric data by Kelley (3) and Stull and Sinke (4). The thermal expansion data are from the measurements of Pearson (7) and Bernini and Cantoni (8).

In Table 1 we have collected the data for evaluating the last term in equation (13), which according to (12) is β/V at 0°C. We can ignore the fact that the compressibility coefficients κ are mostly determined at room temperature instead of 0°C. The values obtained in this way for the free part of the atomic volume, β/V , do not differ too much from the values obtained from melting data in the earlier paper (1) for the face-centered cubic metals Cu, Ag, Au, Zn, and Pb. For Li and Na, however, the new values, 0.39 and 0.32, are much smaller than the values 0.65 and 0.43 obtained from melting data. In fact, it was found in the second paper (2) that the melting data give too high values for alkali metals, probably because of a structural change in connection with fusion.

Table 2 gives in the first column the mean temperatures for the ranges in which

Table 2. Data for calculation of the energy of activation E .

	$^{\circ}\text{C}$	$\Delta U / \frac{\Delta V}{V_0}$ kcal/mole	$\frac{V - \beta}{V}$	E calc. kcal/mole	E obs. kcal/mole	References
Li	100	18.9	0.61	11.5	10	(9)
Na	50	17.5	0.68	12	10.5	(10)
W	2200	196	0.75	147	142	(11)
Cu	850	58	0.81	47	48	(12)
Ag	850	52	0.84	44	46	(12)
Au	850	61	0.86	52	52	(12)
Al	500	40.4	0.83	33	33	(13)
Pb	220	36	0.85	30	28	(14)

the activation energies are determined. The second column gives the value of the first factor of equation (13) at this temperature. The third column gives the second factor, and the fourth the calculated value of E . The fifth column gives observed values of E from the literature. The values for Na, Cu, Ag, Au, and Pb are from self-diffusion measurements, the one for Li from nuclear resonance data, and those for W and Al are extrapolated from diffusion measurements on dilute alloys.

The differences between calculated and observed values for E are well within the limits of the experimental errors. It is hoped that these results will encourage attempts to examine whether the gap left in the present paper, a theoretical foundation of equation (2), can be filled by a statistical treatment of the fluctuations.

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